SURVIVABILITY • SUSTAINABILITY • MOBILITY
SCIENCE AND TECHNOLOGY
SOLDIER SYSTEM INTEGRATION

TECHNICAL REPORT
NATICK/TR-98/013

AD______________

EVALUATION OF CANDIDATE COATINGS FOR THE METAL TRAYCAN

By
George Dittmeier

March 1998

FINAL REPORT
October 1989 - September 1990

Approved for Public Release; Distribution Unlimited

UNITED STATES ARMY SOLDIER SYSTEMS COMMAND
NATICK RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
NATICK, MASSACHUSETTS 01760-5018
SUSTAINABILITY DIRECTORATE

19980417 166

DTIC QUALITY INSPECTED 4

DISCLAIMERS

The findings contained in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

DESTRUCTION NOTICE

For Classified Documents:

Follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For Unclassified/Limited Distribution Documents:

Destroy by any method that prevents disclosure of contents or reconstruction of the document.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	March 1998	Final Oct 89 - Sep 90

4. TITLE AND SUBTITLE

Evaluation of Candidate Coatings for The Metal Traycan

5. FUNDING NUMBERS

OMA PR 728012.19
WU 9315746523000

6. AUTHOR(S)

George Dittmeier

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Soldier Systems Command
Natick Research, Development and Engineering Center
ATTN: SSCNC-WRP
Kansas Street
Natick, MA 01760-5018

8. PERFORMING ORGANIZATION REPORT NUMBER

NATICK/TR-98/013

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The purpose of this study was to obtain quantitative data on the protective properties of coated tin-plated steel traycans versus coated tin-free steel traycans. Four interior coating variables and a control were tested using electrochemical techniques. The study is divided into two parts: Part A - Investigation of Organic Traycan Coatings, and Part B - Investigation of Corrosion Protection of Coated Tin-Plate versus Coated Tin-Free Steel Substrates. Under Part A, three basic assessments were conducted on the organic coatings: 1. electrochemical quantitative assessment of defect, 2. intrinsic protective property assessment using alternating current impedance techniques, and 3. assessment of blister defects in coatings that are indicative of corrosion. The results showed that the candidate coating, Dexter-Midland Matte Sheet, was the superior coating in terms of least number of defects of all the coatings assessed. Based on the alternating current impedance evaluation, the Valspar coating over tin-plate coil stock had the best resistance to penetration by the test corrosion medium. It was determined that blistering occurred after thermoprocessing and that blisters are the sites of future corrosion. Under Part B, accelerated corrosion tests were performed on coated tin-plated steel and coated tin-free steel with intentional defects (i.e., scratches) in contact with various foods. The galvanic current generated between steel and tin in these foods was also measured. Results showed that the tin-plated substrate provided two to three times more corrosion protection than the tin-free substrate, and that the greater the galvanic current, the greater the relative protection provided by the tin-plate.

14. SUBJECT TERMS

COATINGS	PROTECTIVE PROPERTIES	TIN PLATING
TRAYCAN	CORROSION PROTECTION	TIN-FREE STEEL
STEEL TRAY	PENETRATION RESISTANCE	THERMOPROCESSED FOODS

15. NUMBER OF PAGES 57

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

CONTENTS

CONTENTS (CONTINUED)

FIGURES

TABLES

PREFACE

This technical report details the U.S. Army Soldier Systems Command (SSCOM), Natick Research, Development and Engineering Center's (NRDEC) evaluation of candidate coatings for metal traycans used in military group feeding. The report covers the investigation of interior organic traycan coatings as well as the corrosion protection offered by coated tinplate and tin-free steal substrates. Results of the evaluations, conclusions and recommendations are contained within.

The evaluations outlined in this report were conducted during October 1989 through September 1990.

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

SUMMARY

This technical report outlines the investigation of interior organic coatings for traycans (four candidate coatings and a control) designed to contain thermoprocessed foods (Part A), and the corrosion protection offered by coated tin-plated steel traycans versus coated tin-free steel traycans (Part B). In Part A, electrochemical techniques including Enamel Rating and Alternating Current (AC) Impedance Tests were used to evaluate and determine the best coating system among four candidate coatings and a control. Enamel Rating test results indicated that the coating that had the fewest defects is the Dexter Midland Sheet coating. Results of the AC Impedance Tests indicated that the Valspar Matte Coil coating was superior to the other three candidates in terms of its resistance to high-acid and high- salinity foods, but only prior to thermal processing. A further evaluation of blisters on the inside coating of steel traycans indicated that defects may be caused or enhanced by such factors as thermal processing, storage temperature and storage time. In Part B, galvanic and accelerated corrosion studies were conducted to determine the relative effect of a tin-plated versus tin-free steel on protecting coated traycans from corrosion. The galvanic and accelerated corrosion test results demonstrated that tin-plate was more protective than tin-free steel in all instances except in some cans containing foods with very weak galvanic currents. The work confirmed that the degree of protection provided by tin-plating depended in large part on the strength of the galvanic current.

EVALUATION OF CANDIDATE COATINGS FOR THE METAL TRAYCAN

PART A. INVESTIGATION OF ORGANIC TRAYCAN COATINGS

SECTION 1. ENAMEL RATINGS OF STEEL TRAYCAN INTERIOR COATINGS

Introduction

The Enamel Rating test method was used to evaluate four candidate coatings for tin-plated (TP) steel traycans and compare them to a coated tin-free (TF) steel traycan which was used as a control. The candidate coatings include Dexter Midland Matte Sheet (DMS), Reliance Matte Sheet (RMS), Valspar Matte Sheet (VMS), and Valspar Matte Coil (VMC). The tin-free control (CTR) coating was also manufactured by Valspar. Descriptions of each candidate coating and the CTR traycan are outlined in Table 1. Enamel ratings will indicate the total degree of defects in each type of coating and the location of major breaks in the coating. The Enamel Rater test instrument is designed on the principle of applying an electrical potential across the interior of a coated metal food can containing an electrolyte, and measuring the amount of current leakage through the interior of the can through defects or breaks in the coating. The current level in milliamps (mA) is a quantitative measure of the defects in the coating. The Enamel Rating test is used by most can manufacturers, including Silgan Can Co., Ocoromnoc, WI, Central States Can Co., Massillon, OH, and American National Can Co., Barrington, IL Silgan uses the Enamel Rater as a quality control (QC) instrument, where a can having a rating above 5 mA is considered basis for rejection.

Table 1. Description of Test Traycan Coatings

Designation	Exterior Coat	Base Coat	Interior Coat
DMS*	Aluminum Vinyl	Epoxy Phenolic	Aluminum Vinyl
RMS*	Aluminum Epoxy	Clear Epoxy	Aluminum Vinyl
VMS*	Clear Epoxy	Clear Vinyl	Aluminum Vinyl-High Solids
VMC*	Clear Epoxy	Clear Vinyl	Aluminum Vinyl - High Solids
CTR (TF)	Clear Epoxy	Clear Epoxy	White Vinyl

* Tin-Plate Substrate - 90 lb. per base box Electrolytic Tin-Plate, Matte Finish, 0.75/0.35 tin weights.

Experimental Procedure

A total of 2024 stressed cans were removed from long-term storage for the enamel rating evaluation. The objective of this evaluation was to establish which coating demonstrated the fewest number of defects after thermal processing and storage. The testing solution was one percent sodium chloride (NaCl) in tap water. The instrumentation used was the Enamel Rater manufactured by the Wilkens-Anderson Company, Chicago, IL. The circuit consists of a central cathode electrode with the metal traycan as the anode. The instrument is adjusted using the one percent NaCl testing solution to a fixed voltage of 6.3 volts. The test traycan is filled with the testing solution to within one-eighth inch of the top of the can, and with the power on, a reading in mA is obtained. The current level is indicative of the number of defects or breaks in the coating. The traycan interior coatings are evaluated by recording the enamel rater readings or total current draw in mA, and tabulating it against the frequency of readings per current level. The greater the current reading, the greater are the total number of defects. Blisters that are not broken or perforated would not be counted by the enamel rater as defects. Only those blisters that are perforated register. The location of defects is ascertained by reversing the current direction, thereby making the traycan cathodic. Defects in the coating are indicated by hydrogen gas effervescence at the coating break.

Results

Enamel ratings for all traycans examined, stored at all temperatures, are recorded in Table 2. Enamel ratings for traycans stored only at 100 °F are shown in Table 3. This data was tabulated separately to determine if storage temperature had any effect on defects detected by the enamel rater. Defect locations were plotted on traycan maps shown in Figure 1. The enamel rating results indicate that DMS and CTR coatings had the least number of defects. However, when both DMS and CTR coatings were further examined (as described in Section 3), it was noted that the CTR-coated cans had a high number of blister formations in comparison to DMS.

Table 2. Enamel Rater Readings - All Traycans at All Storage Temperatures

Traycan	Frequency of Readings per Current Level (mA)						No. Trays	% at 0-5
Designation	0-5	6-9	10-15	16-20	21-25	>25	Tested	mA (accept)
DMS	310	26	18	10	7	10	381	81.4
RMS	231	49	61	19	46	44	450	51.3
VMS	177	63	55	23	20	13	351	50.4
VMC	206	61	57	15	30	4	373	55.2
CTR	376	19	42	4	18	10	469	80.2
TOTAL							2024	

Table 3. Enamel Rater Readings - Traycans Stored at 100°F

Traycan Designation	Frequency of Readings per Current Level (mA) 0-5	6-9	10-15	16-20	21-25	>25	No. Trays Tested	% at 0-5 mA (accept)
DMS	157	12	11	6	6	-	192	81.8
RMS	91	25	21	9	6	3	155	58.7
VMS	76	25	16	8	10	1	136	55.9
VMC	114	14	22	10	11	2	173	65.9
CTR	176	11	23	4	7	-	221	79.6
TOTAL							877	

Conclusion

Since DMS had the fewest number of perforated defects in comparison to the other three candidate coatings, and the least number of unbroken blister formations, it was concluded that DMS was the best coating system in terms of fewest defects. This was true for all trays stored at all temperatures, including trays at 100°F storage. The DMS coating consistently had the fewest number of defects, followed by CTR, VMC, RMS and VMS. Cans with RMS coatings had the highest percentage of ratings over 25 mA.

INTERIOR DEFECTS

PRODUCT OMELET
TEMPERATURE 100 degrees F

DATE 29 May 1990
WEEK/SAMPLE #1620/RMS

Map VIEWS

[1] Top side - nomenclature facing you
[2] Bottom side - nomenclature facing you
[3] Front side
[4] Back side
[5] Left side
[6] Right side

DEFECTS | X DEFECT LOCATION

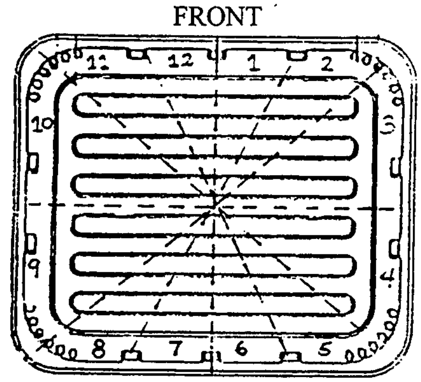
J. Pitted corrosion
K. Blister
L. Scratch
M. Other (effervesence indicating defect penetration to substrate)

REVERSE CURRENT RESULTS
10 mV - Direct Enamel Rater Reading

TYPE K VIEW/LOC 5-7-M
TYPE ______ VIEW/LOC______
TYPE ______ VIEW/LOC______
TYPE ______ VIEW/LOC______
TYPE ______ VIEW/LOC______

[3]
FRONT

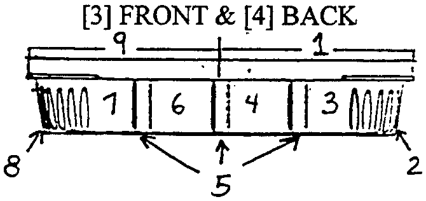
[5] LEFT



RIGHT [6]

BACK
[4]

[3] FRONT & [4] BACK



[5] LEFT & [6] RIGHT

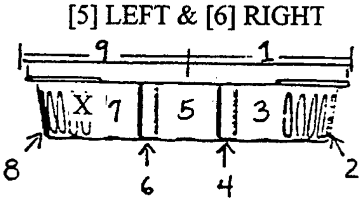


Figure 1. Sample of Interior Defects Map

SECTION 2. ALTERNATING CURRENT IMPEDANCE TESTING OF TRAYCAN INTERIOR COATINGS

Introduction

Alternating Current (AC) Impedance Testing is a sensitive technique commonly used to measure the corrosion resistance of a can coating to food constituents. This section summarizes the work done by Cortest Columbus Technologies, Columbus, Ohio under NRDEC Contract DAAK-60-90-1301[1]. Under this contract, the relative corrosion resistance of the four candidate coatings exposed to a simulated food environment was compared to the CTR. The use of the AC Impedance technique as a QC tool for traycan coatings was also examined.

Experimental Procedure

The type of apparatus used by the contractor is depicted in Figure 2. It consists of a frequency response analyzer used in conjunction with a potentiostat connected to a microcomputer (not shown) for data analysis and plotting. For the NRDEC contract, the test cell shown in Figure 2 was replaced with an empty, unprocessed traycan partitioned into three areas by means of plexiglass dividers and foam gaskets to represent different configurations of the traycan surface. The test areas were filled with a three percent solution of NaCl in distilled or deionized water, adjusted to a pH of 4 to 5 with citric acid to simulate a food environment. The four candidate coatings and the control were evaluated (described previously in Table 1). A series of small AC voltages less than 20 millivolts (mV) were applied to the coated specimen by means of a platinum counter-electrode. Using the signals generated by the potentiostat, the Frequency Response Analyzer produced the corresponding lead or lag angle (phase shift similar to power factor), and the AC Impedance (similar to Direct Current [DC] resistance) at each frequency of applied AC voltage. The computer plotted these data for each exposure time being measured. This plot is called a Bode Plot and is shown in Figure A-1 of Appendix A. Polarization, or total resistance, is obtained from the Bode Plot by extrapolating impedance values for each series of variable frequency measurements on a coating at the low frequency limit. Polarization data is plotted for each coating versus time for 500, 1000, and 1500 hour exposure periods. Polarization, or total resistance, is inversely proportional to the corrosion rate.

Results

The results of the AC Impedance test are plotted in two ways: 1) total or polarization resistance for each coating versus time, and 2) total or polarization resistance for each coating after specific time periods (500, 1000, and 1500 hrs). Figures A-2 through A-6 in Appendix A show the change in polarization resistance with time of exposure in the test environment. Plots that show a high initial resistance with little or no decline over time are indicative of very good coating performance. Figures A-7 through A-9 in Appendix A sum up the relative total system or polarization resistance of all the coatings tested after 500, 1000, and 1500 hours of exposure to

the test environment. The longer exposure data shows the most significant change in polarization; however, not all the coatings were tested for 1500 hours due to budgetary limitations.

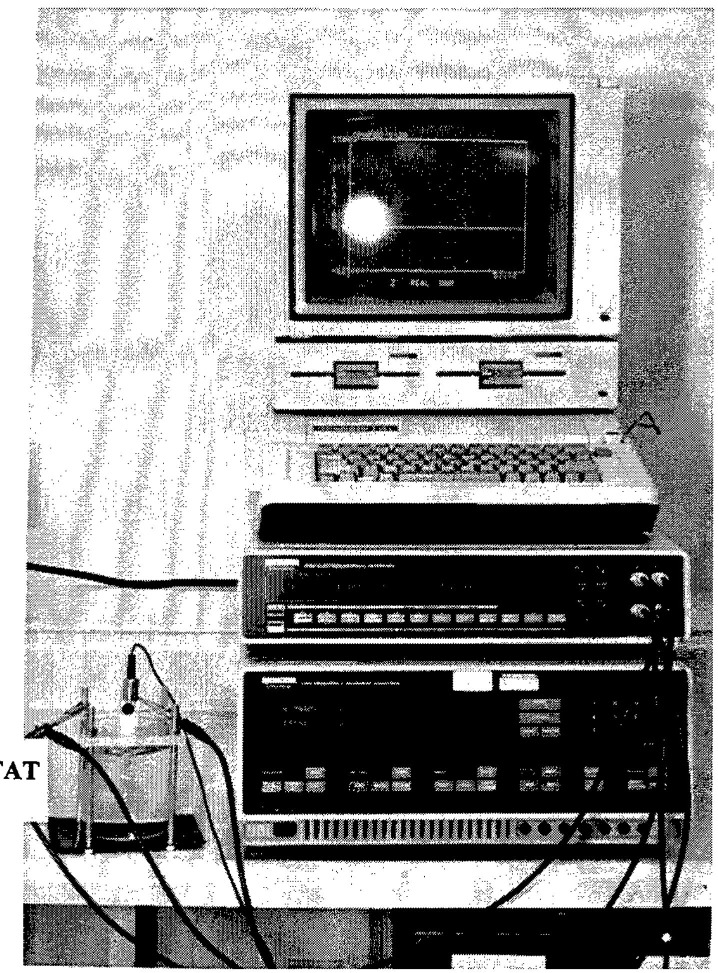


Figure 2. Apparatus Used for AC Impedance Testing

Of the coatings analyzed, the VMC coating was found to be the most resistant to corrosion, followed closely by the DMS and the VMS coatings. The CTR coating had the poorest performance of the coatings analyzed. It should be noted that these results are based on extended ambient temperature exposures of unused, unprocessed traycans and do not take into account any blistering or coating degradation that may be caused by thermal processing or high temperature storage.

Conclusion

The AC Impedance technique produced useful information on the basic corrosion resistance of the traycan candidate coatings versus the CTR. The results showed that the VMC coating on unstressed traycans performed best, with the DMS and VMS coatings following closely behind. The RMS coating was intermediate in performance and the CTR coating had the poorest in performance in terms of corrosion resistance. It should be noted, however, that the AC impedance method should only be used in conjunction with other test methods. For example, even though VMC was the best performer on unstressed traycans based on AC impedance testing, it had more blisters and defects after storage in stressed traycans coated with DMS.

The value of the AC impedance technique is that it can produce data on the comparative intrinsic protective properties of candidate coatings prior to filling the cans, such as pore formation, ionic and electron penetration through the coating, and the effect of moisture absorption, without a costly and time-consuming storage study. Traditional DC polarization electrochemical accelerated test methods cannot be used to evaluate coatings in a corrosive medium. The high resistance of most coatings to imposed DC voltages makes the acquisition of useful data on the system impossible. The AC impedance technique overcomes the problem of high coating resistance and produces useful data on coating performance. By simplification steps described in the contractor's report, coating film permeability, substrate composition, interaction of the substrate with the coating (e.g., adhesion), and corrosion reactions at the substrate can be calculated as total or polarization resistance and plotted versus time[1]. The gradual loss in film adhesion is also shown as declining resistance. Obviously, the higher the total resistance at a given time interval and the less decline with time, the better the coating.

There is possibly some benefit to using the AC Impedance Technique as a QC tool for examining traycan coatings. However, as suggested in the contractor's report, one would first need to investigate methods for reducing the number of test steps, the length of testing and the cost to make the AC Impedance technique a practical QC tool[1].

SECTION 3. EVALUATION OF BLISTERS ON TRAYCAN INTERIOR COATINGS

Introduction

The purpose of this investigation was to examine the characteristics of blisters on candidate coatings and the control traycans that had been subjected to long term storage with representative food products. Blisters on the interior enamel coating of steel traycans are thought to be the initiation locations of traycan perforations known as "grey spots"[2,3]. A typical blister is shown in Figure 3a and a burst or perforated blister is shown in Figure 3b.

Real-time storage studies of filled, sealed and processed traycans conducted at NRDEC produced the following blister data and observations[2]. The coatings with the highest percentage of blisters versus total defects in descending order were CTR, RMS, VMS, VMC and DMS as shown in Table 4. Approximately 95% of defects were determined to be actual blisters. The bar graphs shown in Tables B-1 to B-3 in Appendix B also show rankings for percentage of total blisters (% of major defects) for each type of coating system at 5-1/2 months storage at all storage temperatures.

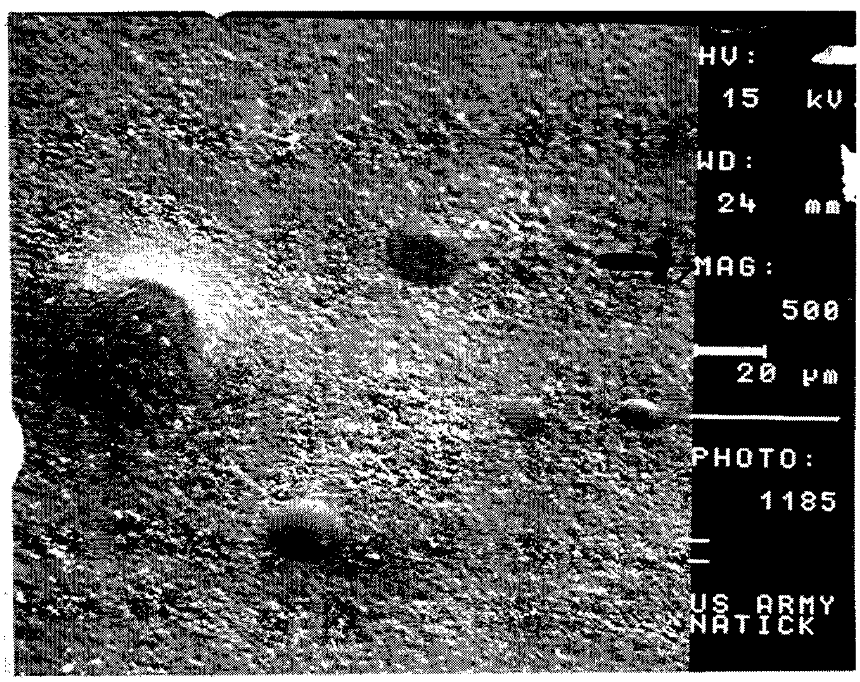


Figure 3a. Photomicrograph of Unperforated blisters on Traycan

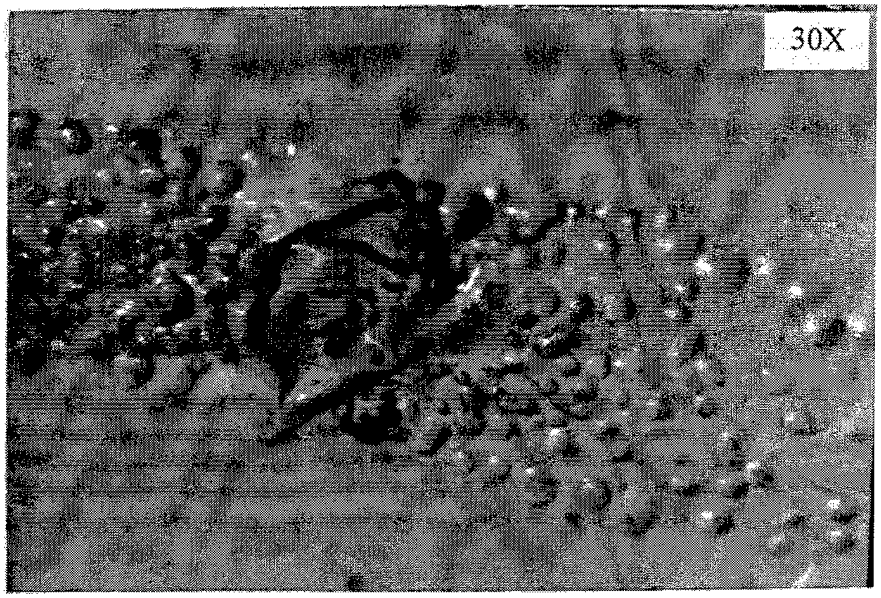


Figure 3b. Photomicrograph of Perforated Blister with Corrosion on Traycan

Table 4. Traycans with Coating Defects
After 5-1/2 Months Storage at All Temperatures [2]

Coating Type	No. of Traycans With Defects	Percent Defective Traycans w/Blisters
RMS	330	55
Control (TF)	270	93
VMS	260	70
VMC	240	41
DMS	100	30

Many other observations were made about blister formation during the Phase I storage study. It was noted that blister formation was potentially exacerbated by the following four factors:

(1) Thermoprocessing. Evidence by the formation of blisters almost immediately (within two weeks) after thermoprocessing. Blisters were virtually non-existent on virgin traycans.

(2) Time of Storage. Evidenced by an increase in blisters with time.

(3) Type of Food. Evidenced by blister formation in various coatings in cans containing specific foods. The number of blisters increased over time with certain types of food and some foods promoted more blisters than others.

(4) Storage Temperature. Evidenced by an increase in blistering in cans stored between 40°F and 80°F. Differences in percent blistering at 80°F versus 100°F varied.

Of all the factors, the most significant cause of blister formation was determined to be the length of storage time. All the other factors were of comparatively lesser importance. The time of storage data indicated that moisture penetration into the blister occurred with time, and opened up blisters at coating locations where there was poor adhesion. Thermoprocessing was considered the next most significant cause of blisters since blisters only occurred after thermoprocessing.

Experimental Procedure

This current evaluation consisted of the following efforts: a determination of the percentage of perforated blisters on thermally processed traycans from SSCOM (NRDEC's) long term storage study using the enamel rater; a determination of the location of blisters and whether or not they are associated with highly stressed coating areas; a scanning for blisters on unprocessed, virgin traycans using the Zorelco Flaw Detector; and accelerated corrosion tests to determine if unperforated blisters are potential sites of perforation after inducing corrosion.

Determination of Percentage of Blisters with Perforations. The Enamel Rater evaluations of traycans described in Section 1 included a reverse current procedure for determining whether or not defects in the interior coating of a traycan had penetrated to the substrate. This procedure was used to determine the percentage of blisters that had perforated in cans after 6 months of storage. The defects map (Figure 1, Section 1) illustrated a typical example of this determination.

Location of Blisters on Traycans from Storage. The Enamel Rater test described in Section 1 was also used on traycans from storage to establish the location of blisters and to determine if they occur more often in highly stressed areas (corners, trims, edges, ribs) or on flat surfaces of the traycan.

Scanning for Blisters on Unprocessed Traycans. Fifteen virgin trays with the four candidate coating variables and the control were evaluated using the Zorelco Model 269 PHD Coating Flaw Detector. This instrument operates on the same principle as the Enamel Rater except that results are qualitative rather the quantitative. The readout is an alarm to denote a defect. The

device consisted of a wetted sponge which is rubbed over the coating, a lead to the bare coated metal and a battery. Voltages were adjustable. When the circuit is completed by a flaw penetrating to the metal substrate, the alarm sounds. The instrument can be increased in sensitivity by increasing the voltage (range 9-90v). However, higher voltages can cause coating penetrations at weak coating areas (thin coating, poor bond) and should not commonly be used.

Accelerated Corrosion Test on Unperforated Blisters. A limited accelerated corrosion test was performed on a RMS traycan that had been filled with corn and stored for 5 months at 100°F. The can contained eight blisters without perforations. The test was carried out in the same manner as later described in Part B, Sections 1 and 2 on galvanic and corrosion experiments on various foods in traycans. The medium used was three percent salt solution derated with nitrogen. An imposed voltage of 400 mV was applied. The accelerated test duration was 77 hours. The blisters were then reexamined for perforations using both the Zorelco Flaw Detector and the Waco Digital Enamel Rater instruments.

Results

Determination of Percentage of Blisters with Perforations. Enamel rater data on 317 blisters in 1,000 traycans were analyzed. The data showed that after 6 months of storage, 35 percent of the blisters were perforated and 65 percent were intact. The CTR had the greatest number of perforated blisters while DMS had the least.

Location of Blisters on Traycans from Storage: The results of this investigation showed that approximately 15 percent of the blisters occurred on highly stressed areas such as ribs, edges and rims of the traycans. Eighty-five percent of all blisters occurred on flat surfaces of thermoprocessed traycans.

Scanning for Blisters on Unprocessed Traycans. Table 5 presents the results of defects on virgin, unprocessed traycans detected by the Zorelco Flaw Detector. The defects detected were characterized as mars or scratches that penetrated to the substrate. Blister perforations were detected on only one of the candidate coatings the RMS.

Accelerated Corrosion Test on Unperforated Blisters. After five months storage at 100°F, evaluation of blisters on RMS traycans filled with corn showed no perforations on any of eight blisters found before accelerated testing. However, after 77 hours of accelerated corrosion testing, five of the eight blisters perforated with ensuing corrosion. No further perforations occurred on surrounding areas. Although this test was limited to only one can with eight blisters, accelerated corrosion tests revealed that unperforated blisters on thermoprocessed traycans are future sites for perforation and subsequent corrosion.

Table 5. Results of Defect Test with Zorelco Flaw Detector

Coating Variable	No. Trays Tested	Imposed Voltage 9 V	Imposed Voltage 22.5 V
DMS	1	No defects	No defects
	1	No defects	One scratch
	1	No defects	No defects
VMS	1	No defects	No defects
	1	No defects	No defects
	1	No defects	No defects
CTR	1	No defects	Several scratches
	1	No defects	No defects
	1	No defects	No defects
RMS	1	No defects	No defects
	1	No defects	No defects
	1	One blister	One blister
VMC	1	No defects	One scratch
	1	No defects	No defects
	1	No defects	No defects

Conclusions and Discussion

From the results of physical testing (chemical/electrical/mechanical) and the previous results of the real-time storage study, the relationship between blister formation and traycan grey spots is better understood. Blisters are indicative of poor localized coating adhesion to the substrate, and possibly thinness and other intrinsic defects within the coating[4]. Paradoxically, based on Enamel Rater data, the CTR coating (Valspar) had poor adhesion to the tin-free substrate. The opposite should have occurred since the tin-free substrate is known to have better adhesion properties compared to tin-plate. One plausible explanation provided by industry representatives was that contaminated tin-free substrate treatment caused this problem[5]. Examining the location of blisters showed they do not routinely form over the highly deformed areas of the traycan. Results from the scanning of unprocessed trays showed that blisters form only after filling, processing, and storage of traycans. Although blisters were detected in the RMS coating on an unprocessed tray, this may have been due to the poor quality of that coating as evidenced in all the other tests. Blisters appear to be the major type of coating defect that leads to pitting corrosion and subsequent perforation or grey spots. This was reinforced by the results of the limited accelerated corrosion study which showed that coating perforation and subsequent corrosion occurred only at blister sites, and not in surrounding non-blistered areas. These results confirmed what was observed in previous studies by Ross[2] and Lei [6]. However, blister formation on interior traycan coatings does not necessarily mean perforation will always occur and allow the initiation of corrosion. This is concluded because after 6 months of storage, only 35 percent of the blisters found in the real-time storage test had perforated.

PART B: INVESTIGATION OF CORROSION PROTECTION OF COATED TRAYCANS; TIN-PLATE VS. TIN-FREE STEEL

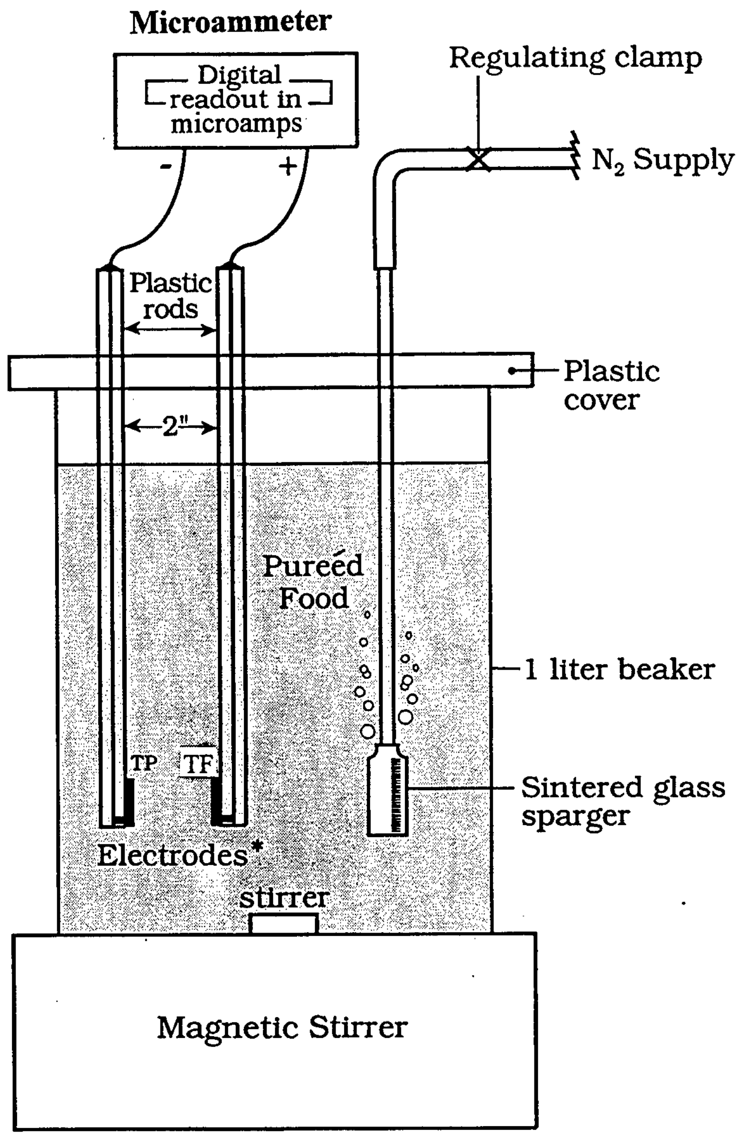
SECTION 1. OPEN SYSTEM: GALVANIC AND ACCELERATED CORROSION SCRATCH TESTS (TIN-PLATE VS. TIN-FREE STEEL)

Introduction

Both galvanic and accelerated corrosion tests were conducted to determine the relative effect of tin-plated versus tin-free steel on protecting coated traycans containing processed foods from corrosion. S.C. Britton showed that high tin/steel galvanic currents correspond directly with the corrosiveness of the food[7]. Can corrosion experts also stated that the protection provided by tin increases with the corrosiveness of food[8]. The objectives of this study were to determine whether tin-plated steel provided more protection in coated traycans than did tin-free steel, and whether there is a relationship between the protection provided by tin and the galvanic current magnitude. This section describes the galvanic and accelerated corrosion scratch experiments performed in an "open system," that is, a simulated traycan comprised of an open beaker and other components as shown in Figures 4 through 6.

Experimental Procedure

Galvanic Tests. The purpose of the galvanic current test is to examine the corrosiveness of different foods used in military rations. This test was conducted on uncoated specimens of tin-plate and tin-free steel. The procedure followed for uncoated samples is outlined in Britton's book Tin Versus Corrosion[7]. The apparatus for testing samples of uncoated tin-plate and uncoated tin-free steel is shown in Figure 4. The apparatus, a Zero Resistance Microammeter manufactured by Keithley Instruments, consists of a cell or beaker containing two electrodes, a nitrogen purge tube, a sintered glass sparger, a magnetic stirrer and a clear plastic cover. The electrodes are attached to each specimen of tin-plated and tin-free steel. The 750 milliliters (ml) of food was pureed in a commercial electric blender, and mixed with an equal amount of tap water to reduce viscosity. The pH was also measured. The food/water mix was agitated with a magnetic stirrer and derated using a nitrogen purge through a sparger. The nitrogen volume was at a moderately high rate of about 1000 cc/min for the first 15 minutes and then reduced to a low flow of about 300 cc/min. Temperature was ambient. The apparatus was covered loosely with plastic to preserve the environment. A minimum test time of 11 hours is required for equilibrium conditions to occur. However, for this test, longer periods of up to 16 hours were used. The DC voltage induced was 1000 mV-1400 mV with specimens anodic.



* - Electrode 1 sq. cm. tin plate (TP);
and electrode 1 sq. cm. tin free steel (TF);
[connections to insulated lead wires
are soldered and coated with epoxy.]

Figure 4. Schematic of Galvanic Test Apparatus, Open System

Accelerated Corrosion Scratch Test. The purpose of the accelerated corrosion scratch test is to examine the degree of protection provided by the tin-plate vs. the tin-free steel. This test was first conducted on coated specimens of tin-plated and tin-free steel. The basic procedure used in this study is based on a similar procedure described by S.C. Britton[7]. In Britton's experiment, the scratch test with imposed current in the anodic direction was applied to test specimens to specifically test for coating undercutting. The NRDEC method was used to specifically examine the comparative protection provided by tin. The apparatus used for NRDEC open scratch tests consisted of applying an anodic current to a scratched coated tin-plate test sample, immersed in a

food product. Figure 5 is a schematic of the Scratch Test Apparatus and Figure 6 depicts the combined Galvanic and Scratch Test Apparatus. A DC power source was used, set between 400 and 1000 mV. Other components of the apparatus are similar to the galvanic test apparatus. For each test specimen, a 1-1/4" long scratch penetrating to the steel substrate is made on the inside coating. The opposite side of the specimen has the soldered connection to the lead wire, and all edges are coated with epoxy. Specimens are connected to the positive or anodic terminal of the DC power source, thereby accelerating corrosion at the scratches. A one-half inch by one-half inch steel sheet is attached to the negative post of the DC power supply by a wire and alligator clip to act as a counter electrode. This electrode is negative and is therefore protected from corrosion. Food is prepared in the same manner as the galvanic tests. A needle nose micrometer (Starrett Model 210-A) was used to measure the depth of corrosion at the scratches. The average test time duration is three and one-half days to obtain a significant difference in corrosion between tin-plate and tin-free steel specimens.

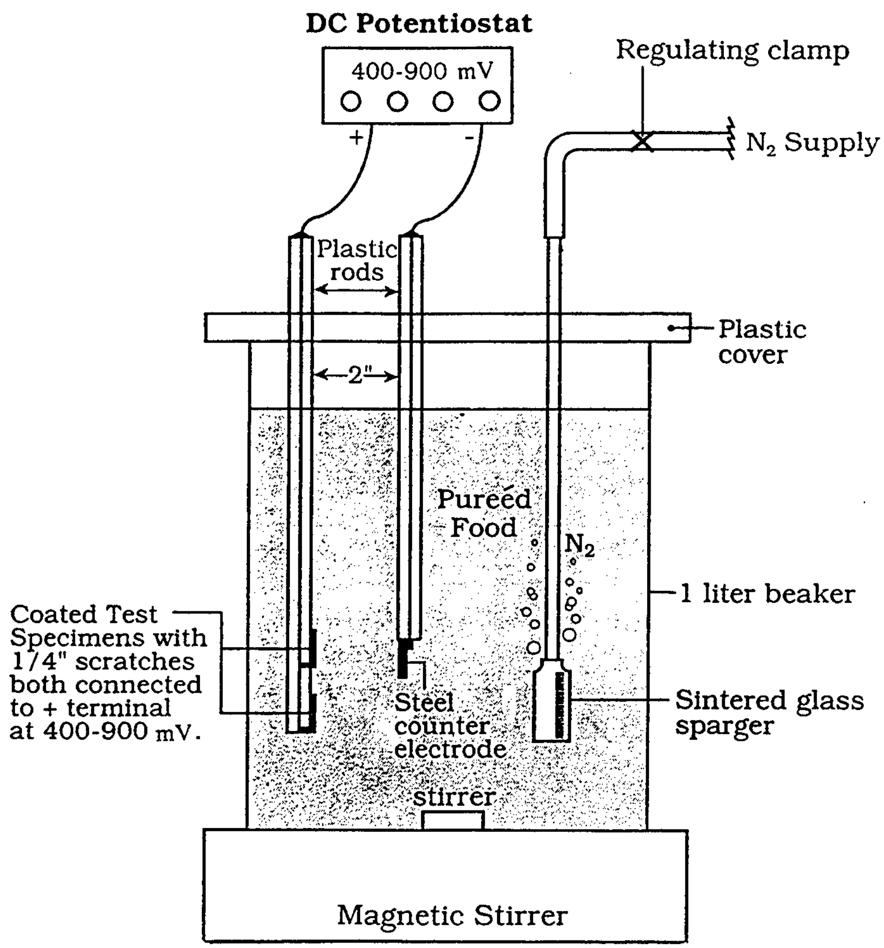


Figure 5. Schematic of Scratch Test Apparatus, Open System

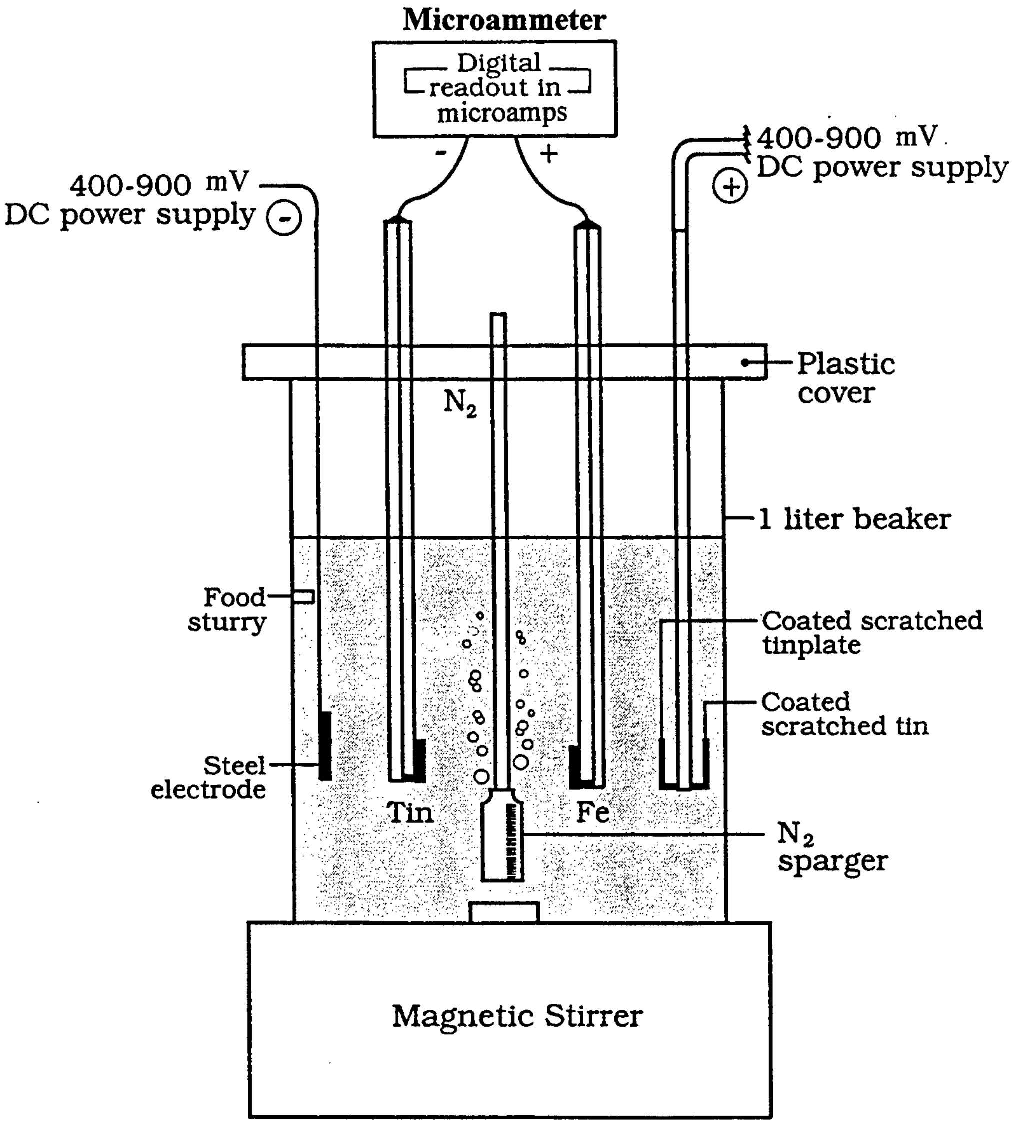


Figure 6. Schematic of Combined Galvanic and Scratch Test Apparatus, Open System

Following the accelerated corrosion test on coated samples, another accelerated corrosion test was conducted on uncoated substrates using a three percent solution instead of food. This test was conducted on uncoated samples to determine how much additional corrosion resistance is supplied by tin-plate vs. tin-free steel. The corrosion resistance was measured by determining weight loss of samples specimens. Specimens were washed, dried and weighed on an analytical scale to the nearest milligram.

Results

Table 6 lists the foods tested in order of corrosiveness as measured by the galvanic current test. Foods with low galvanic currents were considered to be the least corrosive and foods with high currents were considered the most corrosive. Foods were then ranked in terms of corrosiveness, with the most corrosive foods given a ranking of 1.

Table 6. Corrosiveness of Foods

Corrosiveness as Indicated by Level of Galvanic Current	Food	Corrosiveness Ranking
low (-2 to -6 mA)	Meatballs, Rice, Tomato Sauce	6
	Green Beans	5
	Macaroni Salad	4
medium (-7 to -12 mA)	Corn	3
	Chili	2
	Beef Stew	2
high (-13 to -17 mA)	Spaghetti and Meatballs	2
	Carrots	1
	Eggs and Ham	1
	3% Salt Solution (control)	1
	Lasagna	1

Table 7 combines the accelerated corrosion results from scratch tests on coated TP and coated TF steel with the corrosiveness of foods from the galvanic current tests (from Table 6). Results of the accelerated corrosion investigation show that tin-plate provided anywhere from one to six times more corrosion protection than the tin-free substrate. The amount of corrosion protection was determined by measuring the depth of the corroded scratch into the substrate with a needle nose micrometer.

The depth of corrosion is assessed after accelerated testing using a needle nose micrometer. Table 8 outlines the corrosion depth assessment on tin-plated and tin-free steel traycans containing Spaghetti and Meatballs. Table 9 shows the background and weight loss results of accelerated corrosion testing (performed in the same manner as the scratch test) on uncoated tin-free vs. uncoated tin-plated traycans.

Table 7. Corrosion Results From Galvanic Current Test Combined with Scratch Test

Food Tested	Scratch Test Results Most Corroded	Factor (a)	Corrosivity Rank Scratch Test (b)	Avg. Galvanic Current, mA Value	Rating (c)	Galvanic Corrosivity Rank
3% NaCl	TF	3X	1	-16	H	1
Lasagna	TF	4-6X	1	-17	H	1
Eggs & Ham	TF	3X	1-2	-15	H	1
Beef Stew	TF (d)	4-6X	1	-11	H	2
Carrots	TF	2-3X	2	-12	H	1
Chili	TF	3-4X	1	-10	M	2
Spaghetti & Meatballs	TF	3X	1-2	-12	H	2
Corn	TF	1.15X	3	-9	M	3
Macaroni Salad	Neither	-------	3	-5	L	4
Green Beans	TF	1.15X	3	-6	L	5
Meatballs, Rice & Tom	TF	1.15X	3	-2	L	6

a) Factor: Factor by which one substrate corrodes compared to the other (depth of scratch measured).
b) Corrosiveness Rank Scratch Test: ranking of food in accordance with corrosiveness; No. 1 being most corrosive.
c) Average Galvanic Current Rating: ratings base on the following code: 11 mA and above = high (H); 7-10 mA = medium (M); 1-6 mA = low (L).
d) Beef Stew: scratch test result obtained in a closed system.

Table 8. Corrosion Depth Assessment on Coated Traycans

Conditions

Coated specimen size: 2" x 1.5
Coated specimen thickness: 10.5 mils thick including both coatings
Scratch characteristics: 6 scratches, 1.25" long, each scratch 3/8 apart
Food: Spaghetti and Meatballs

Table 8. Corrosion Depth Assessment on Coated Traycans (Continued)

Location No. of scratch	Thickness, mils including outside coating		Depth of Corrosion (mils)	
	Tin-Plate	Tin-Free	Tin-Plate	Tin-Free
1	6	0	4	10
2	3	0	7	10
3	7	7	3	3
4	5	5	5	5
5	4	4	6	6
6	3	7	7	3
		Average:	5	7

Table 9. Accelerated Corrosion Test Results on Uncoated Tin-Plate and Tin-Free Steel Traycans

Specimen[1]	1000 mV, (1-1/4 hr)[2]	1400 mV, (6-1/4 hr)	Total: (7-1/2 hr)
Tin-free	0.118 g[3]	0.209 g	0.327 g
Tin-plate	0.071 g	0.125 g	0.191 g

1/ Specimens: 3.74 square cm sample of tin-free and tin-plated steel without coating.
2/ Induced Voltage: 1000 mV - 1400 mV with specimens anodic
3/ Weight Loss measured in grams

Conclusions

Galvanic Tests: Can corrosion experts and literature indicate that the protection provided by tin increases with the corrosiveness of food. The data obtained from the galvanic tests conducted here suggest the tin-plate does not provide substantial added protection in cans containing products with low corrosiveness, but does appear to provide significant added protection for highly corrosive foods. In general, vegetables in brine have the lowest levels of galvanic current and are considered to be the least corrosive food products. One exception to this is carrots, which are acidic and had a high galvanic current. Foods containing tomato -- such as chili, spaghetti and meatballs, lasagna and beef stew -- were more corrosive and exhibited greater galvanic currents. The galvanic current data on three percent salt solution (Table 6) showed that salt is definitely a factor in corrosiveness, and probably accounted for the high corrosiveness of eggs with ham.

There appears to be a good correlation between the corrosiveness of food and the effectiveness of tin-plate in preventing corrosion, when compared to tin-free steel at defects in the coating.

Accelerated Corrosion Tests: Most of the data from the accelerated corrosion test on coated specimens showed that tin-plate is definitely more protective than tin-free steel under a coating. One exception was macaroni salad which showed no corrosion on either type of substrate over a long test period. Accelerated corrosion tests on the uncoated specimens, to determine how much additional corrosion resistance is supplied by tin-plate vs. tin-free steel, showed tin-plate provides 1.7 times more corrosion resistance than tin-free steel. However, it should be noted that after de-tinning of the tin-plate, this protection will likely disappear.

The galvanic and accelerated corrosion scratch test results demonstrated that tin-plate was more protective than tin-free steel in all instances except possibly those cans containing foods with very weak galvanic currents. The work confirmed, for the most part, that the degree of protection provided by tin-plating depended on the strength of the galvanic current. However, it is also believed that the heavy tin-plate used (.75 lb/bb) was a factor since the protection of the exposed steel where thinner tin-plate is used is severely reduced as it sacrificially corrodes. The galvanic and corrosion scratch tests discussed in this section were also summarized in a NRDEC Memorandum Report on this subject[9].

Recommendations

It is recommended that more work be done using galvanic and scratch tests to examine products with low corrosiveness. It is also recommended that a long term, real time storage study be conducted for three years on traycans with scratches with no imposed current to determine the actual percent of increased protection provided by tin-plate.

SECTION 2: CLOSED SYSTEM: GALVANIC AND ACCELERATED CORROSION SCRATCH TESTS (TP VS. TF STEEL)

Introduction

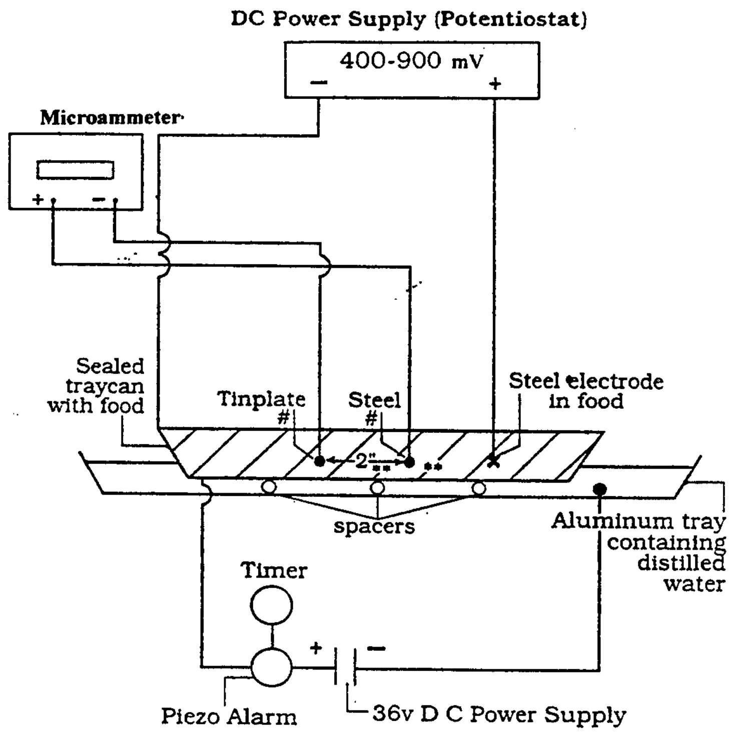
This section covers similar galvanic and accelerated corrosion experimental work performed on enamel coated steel traycans, but in a 'closed system.' A closed system is a simulation of the actual environment inside a filled, sealed and thermoprocessed traycan. Conversely, an 'open system' utilized a simulated open traycan environment involving a vented beaker with nitrogen purge. While the closed system most closely represents the canned food environment, it is difficult and very time consuming to construct and operate closed system tests in the laboratory due to the many steps involved.

Experimental Procedure

Galvanic Tests: Galvanic tests were conducted in the same manner as reported in Part 2,

Section 1, except that the electrodes were sealed inside the food filled traycan as shown in Figure 7. The lead wires were sealed with silicone room temperature vulcanizing cement. Chili, beef stew, green beans and macaroni salad were sealed and thermostabilized inside the traycans which were subsequently attached to the apparatus shown previously in Figure 6. The first product tested, Chili, was done in duplicate to examine reproducibility of results.

Scratch Tests: Scratch tests were performed only on coated traycans in a similar manner as in the open system following the galvanic test. Products tested were beef stew, chili, green beans and macaroni salad. One internal metal electrode (separate from the galvanic electrodes) was attached to the negative power source on the DC potentiostat. The entire traycan was attached to the positive power source, with the potential set between 400 and 1000 mV. This forced the scratches to corrode. When the traycan corroded through at one of the scratches, a leak detector circuit registered the approximate time of leakage by means of both an alarm and time as shown in Figure 7. When the traycan leaked at a scratch, the liquid portion of the food is diluted by the distilled water in the aluminum tray. This causes an increase in the conductivity of the water, closing the highly sensitive circuit between the traycan and the aluminum tray. The alarm is then activated and the timer indicates when the leak occurred.



#-Electrodes (1 sq cm) for galvanic current measurement
**-Two 1.25"-long scratches through coating on bottom

Figure 7. Schematic of Scratch Leak Test Apparatus, Closed System

Results

Galvanic Test: The galvanic test results in the closed system versus the results in the open system are outlined in Table 10.

Table 10. Galvanic Test Results - Closed System vs. Open System

	Closed System		Open System	
Food	Final Reading (mA)	Test Duration (hrs.)	Final Reading (mA)	Test Duration (hrs.)
Chili	-8	16	-11	18
Chili (repeat)	-8	16	-11	16
Beef Stew	-1	14	-11.4	15
Green Beans	-0.7	23	-3.2	22
Macaroni Salad	-0.45	14	-3.5	25

Scratch Test: The scratch test results for the closed system are shown in Table 11. Closed system results were similar to the results obtained in the open system.

Table 11. Scratch Test Results - Closed System

Food	Duration	Results
Beef Stew	1-1/2 weeks	Coated tin-free traycan corroded an estimated 4 times faster than coated tin-plated traycan
Chili	2 weeks	Terminated due to leaks through wire
Green Beans	1 week	Tin-free traycan corroded 1.25 times faster than tin-plated traycan
Macaroni Salad	8 days	Tin-plated traycan corroded slightly faster than tin-free traycan

Conclusions

With the exception of beef stew, there was a fairly good correlation between the galvanic current test results when conducted in an open and closed system. It is possible that the high viscosity of the sauce in the Beef Stew produced a much lower galvanic current in the closed system than in the open system. Scratch test results for the closed system were similar to the results obtained in the open system. As was the case with the open system, the low galvanic current for green beans and macaroni salad (i.e., low corrosiveness) correlated with the low

low protection provided by the tin. Thus, it is concluded that tin-plate does not provide substantial added protection in cans containing products with low corrosiveness. However, tin-plate does appear to provide significant added protection for highly corrosive foods such as the beef stew.

Recommendations

It is recommended that more work involving galvanic current tests be conducted to confirm results obtained in Section 2. Further, several more foods, including those that are highly corrosive, should be tested for corrosiveness on scratched surfaces in the closed system. The leak detector apparatus performed satisfactorily in the closed system and provided a record of the start of a leak. However, future apparatus should be modified to give an earlier warning of the impending perforation at the scratches.

SUMMARY OF CONCLUSIONS

PART A

The Enamel Rater test results for coating defects showed that the DMS coating was superior to the other candidates, followed by the CTR, VMC, RMS and VMS. The RMS and VMS coatings were nearly equal in quality and number of defects.

The AC Impedance test conducted on unprocessed cans in a simulated food environment showed that the VMC coating performed the best, closely followed by DMS and VMS. However, the VMC coated cans had more blisters and defects after processing and storage than the DMS traycan. The CTR coating was demonstrated to be the poorest coating when tested in this manner. It is recommended that the AC Impedance test be used in conjunction with other test methods.

Based on data presented in this report, and previous data reported by Ross[2], it is concluded that the DMS coating system is the best of the five coating systems tested when used with a variety of products.

Blisters on coatings form almost entirely after thermoprocessing of the traycans, increase in number over time, and are the sites of future interior corrosion pitting.

PART B

Results of galvanic current and accelerated corrosion tests showed an average of two to three time greater corrosion protection was achieved by tin-plating the steel substrate when compared to tin-free steel substrate. There is also a slight correlation between enhanced corrosion protection provided by tin-plate when in direct contact with more corrosive foods.

This document reports research undertaken at the U.S. Army Soldier Systems Command, Natick Research, Development and Engineering Center and has been assigned No. NATICK/TR-98/013 in the series of reports approved for publication.

REFERENCES

1. Cortest Columbus Technologies. 1991. AC Impedance Testing of Coated Traycans, Natick TR-93/019, U.S. Army Natick Research, Development and Engineering Center, Natick, MA.

2. Ross, Jeanne M. 1991. Traycans: Tin-plate vs. Tin-Free (Phase I), Natick TR-91/030, U.S. Army Natick Research, Development and Engineering Center, Natick, MA.

3. Dittmeier, George H. 1990. Investigation of the Protection of Steel Substrate Provided on Enameled Traycans, Memorandum Report No. 171, U.S. Army Natick Research, Development and Engineering Center, Natick MA.

4. Munger, C.G. 1984. Corrosion Prevention by Protective Coatings, National Association of Corrosion Engineers, Houston, TX.

5. Dittmeier, G. and Waidzunas, P. 1990. "Blisters on Interior of Traycan Coatings," Record of Conversation between NRDEC and Valspar Corp.

6. Lei, K.S. et al. 1990. Metallurgical Analysis of Leaking Tray Packs, MTL Technical Report TR 90-30, Materials Technology Laboratory, Watertown, MA.

7. Britton, S.C. 1975. Tin Versus Corrosion, International Tin Research Institute, England.

8. Dittmeier, G. and Hultberg, R. 1990. "Blister Formation," Record of Conversation between NRDEC and Wheeling Pittsburgh Steel Corp.

9. Dittmeier, George H. 1991. Galvanic and Accelerated Corrosion Experiments on Various Foods in Enameled Traycans, Tin-Free Steel vs. Tin-Plate, Memorandum Report No. 176, U.S. Army Natick Research, Development and Engineering Center, Natick, MA.

APPENDIXES

APPENDIX A

AC IMPEDANCE TEST FIGURES

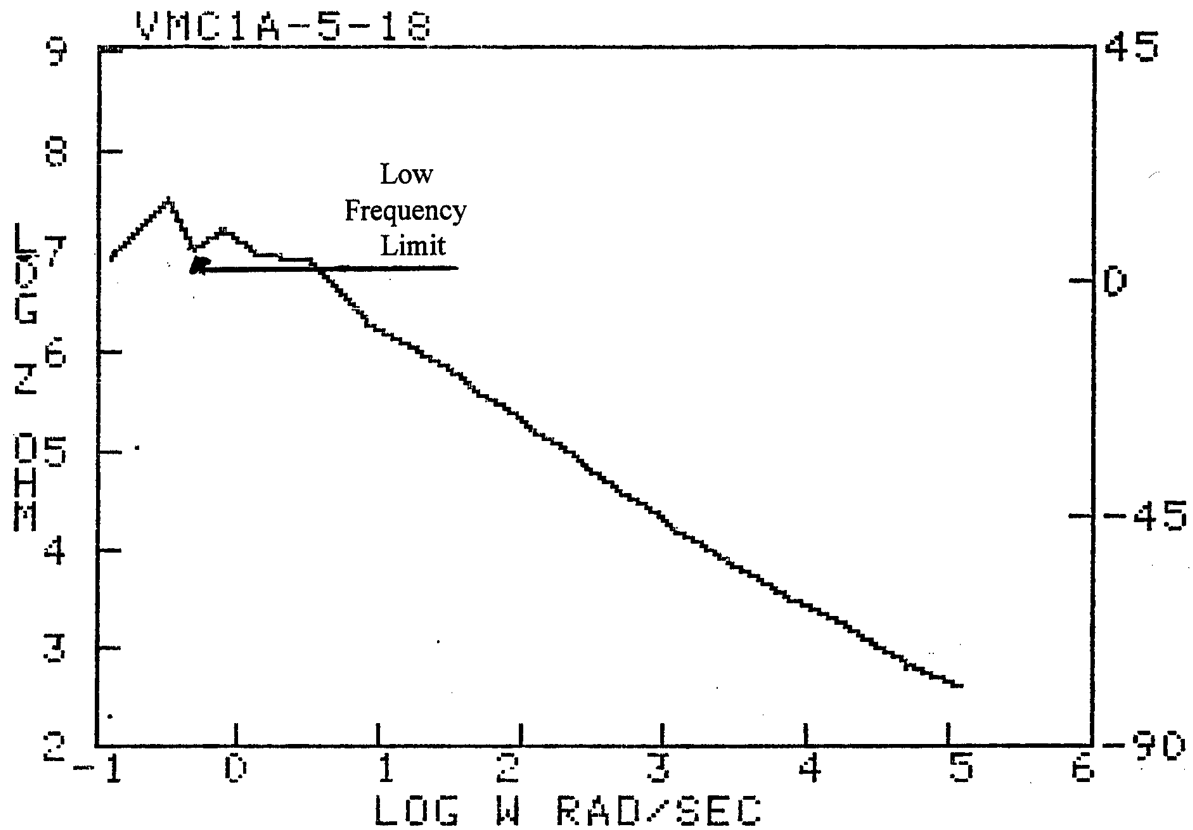


Figure A-1. Bode Plot For VMC Coating After 430 Hours of Exposure

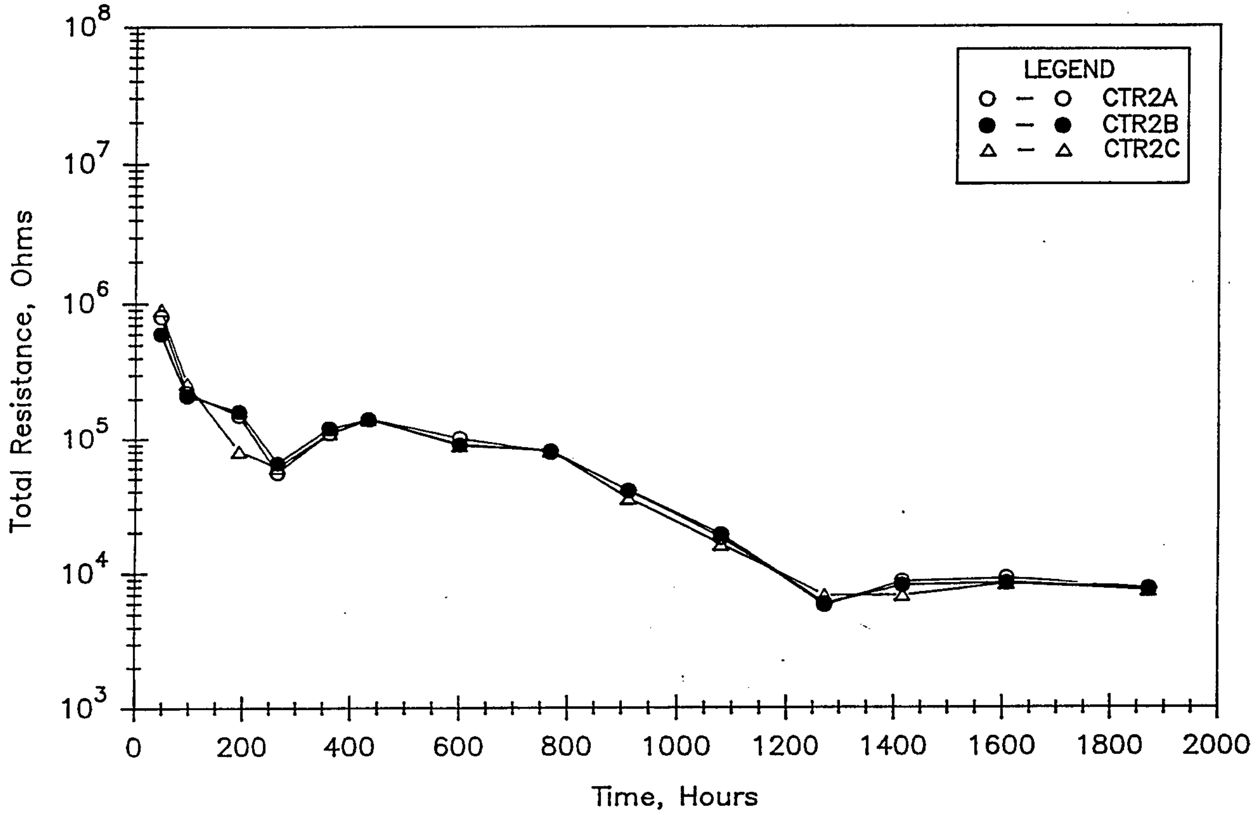


Figure A-2. Total Resistance As A Function Of Time For Control Coating (2). A And C Were Corner Compartments; B Was Center Compartment.

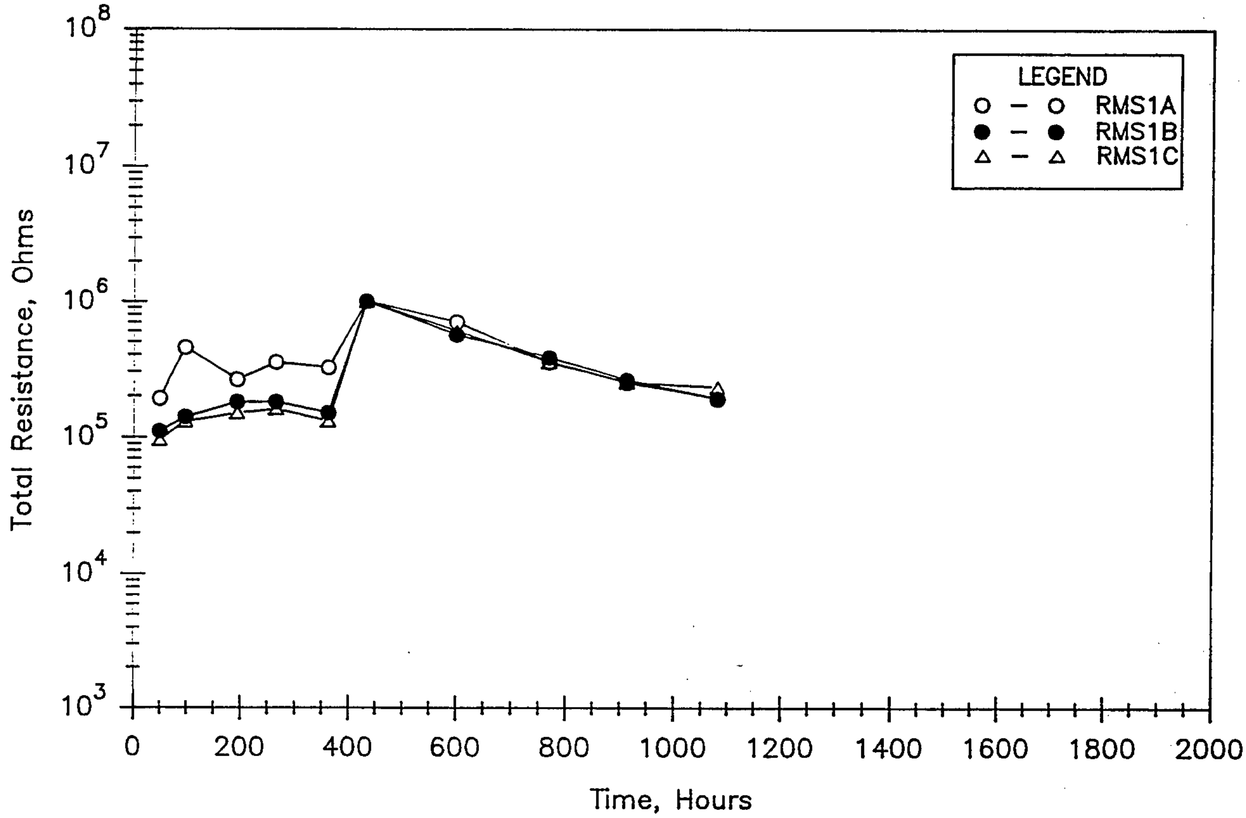


Figure A-3. Total Resistance As A Function Of Time For RMS Coating (1).
A And C Were Corner Compartments; B Was Center Compartment.

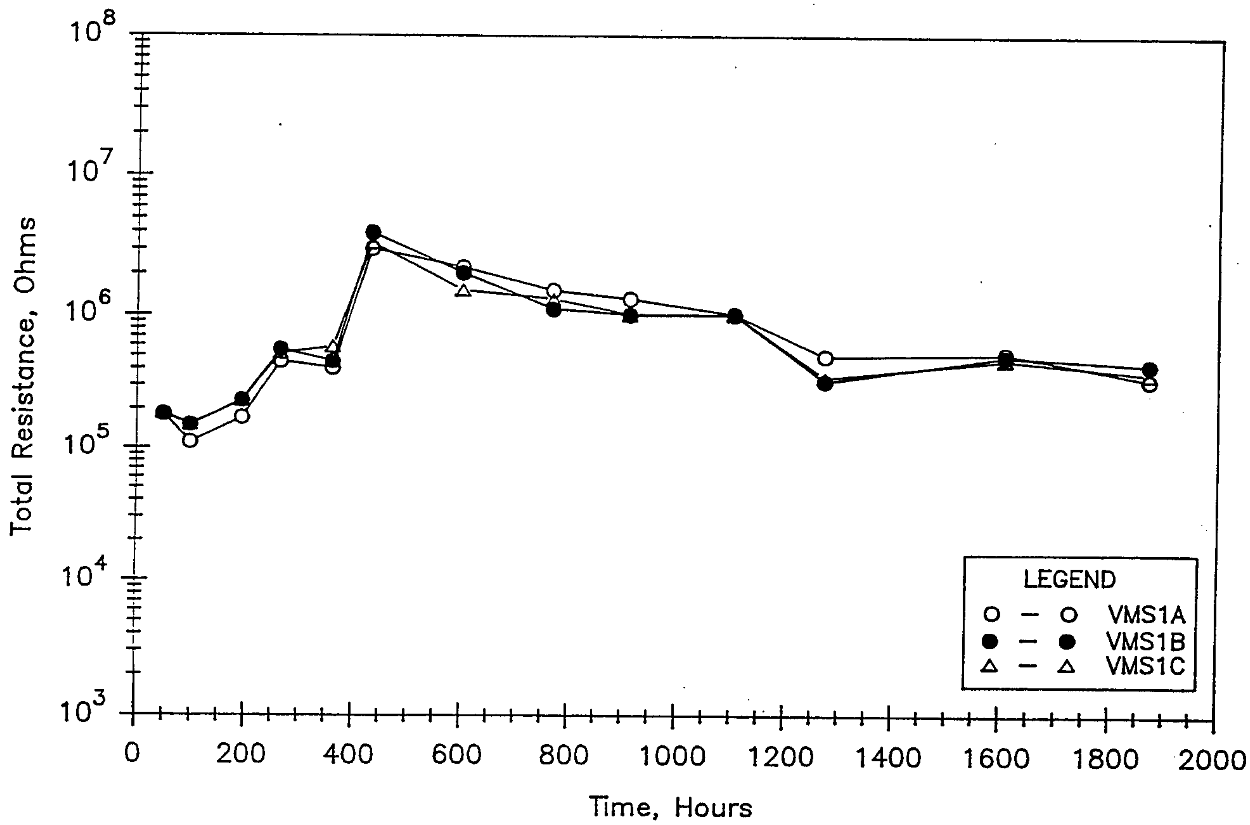


Figure A-4. Total Resistance As A Function Of Time For VMS Coating (1).
A And C Were Corner Compartments; B Was Center Compartment.

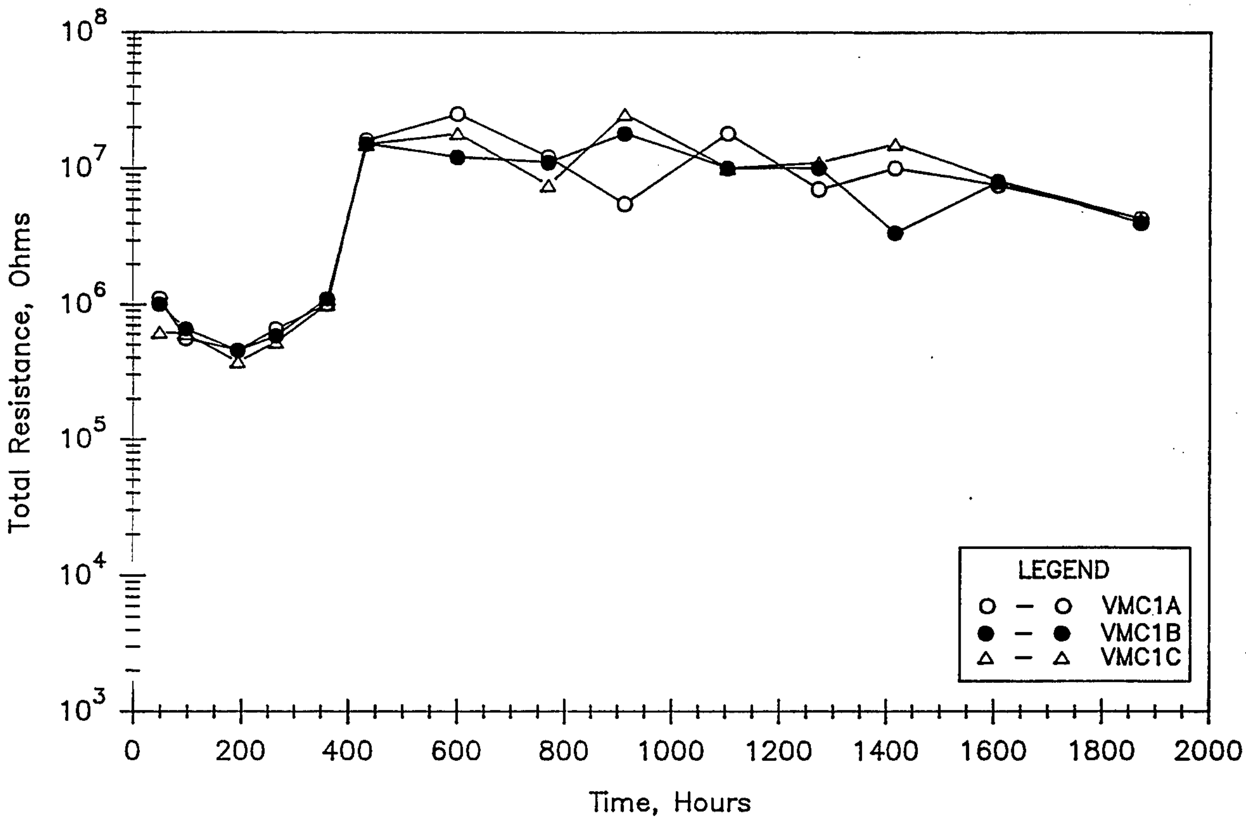


Figure A-5. Total Resistance As A Function Of Time For VMC Coating (1).
A And C Were Corner Compartments; B Was Center Compartment.

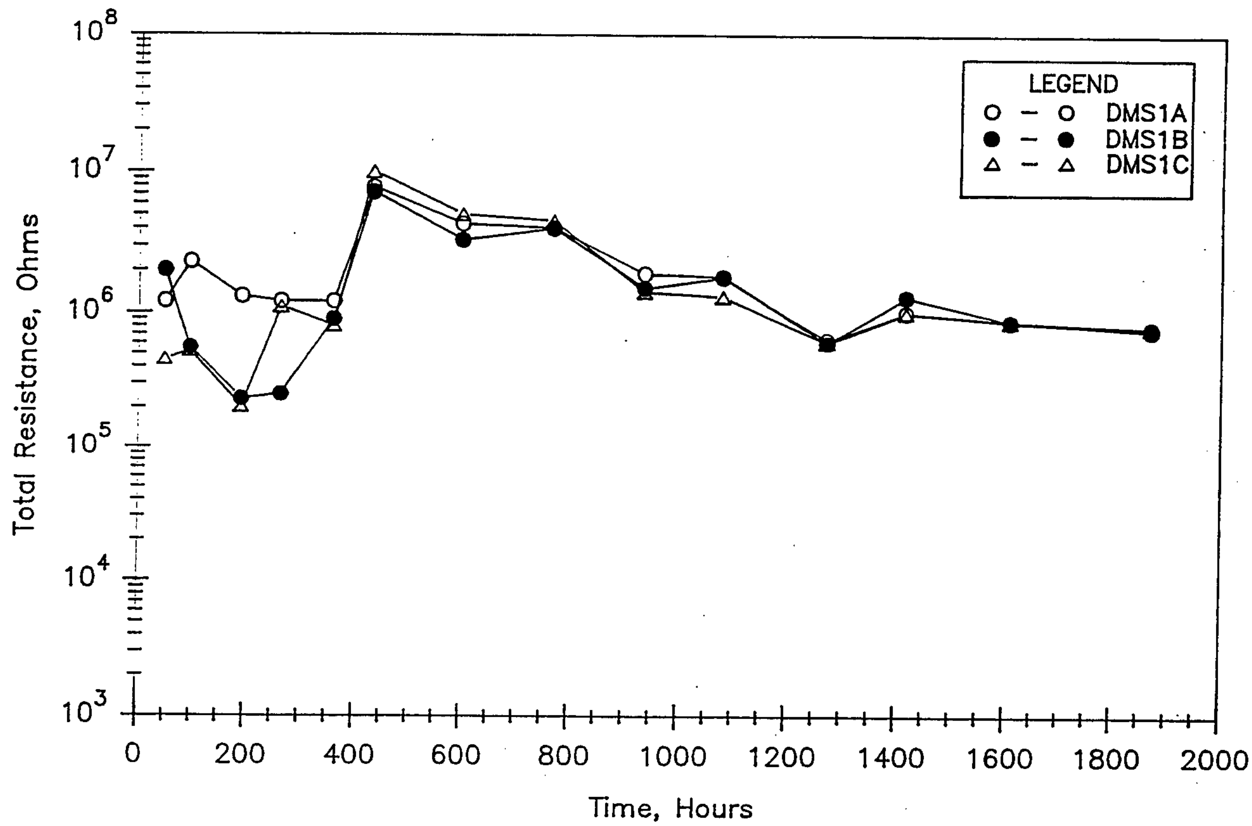


Figure A-6. Total Resistance As A Function Of Time For DMS Coating (1).
A And C Were Corner Compartments; B Was Center Compartment.

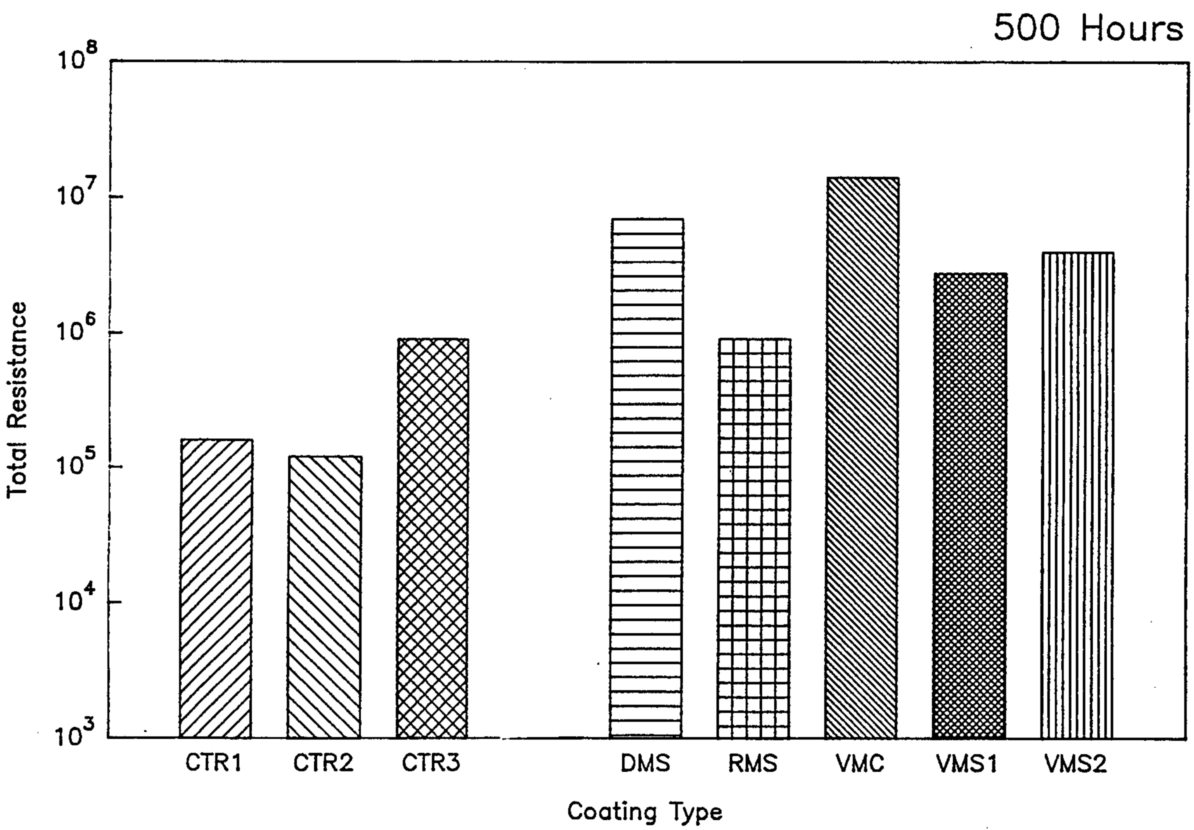


Figure A-7. Total Resistance For Various Coatings After 500 Hours Exposure

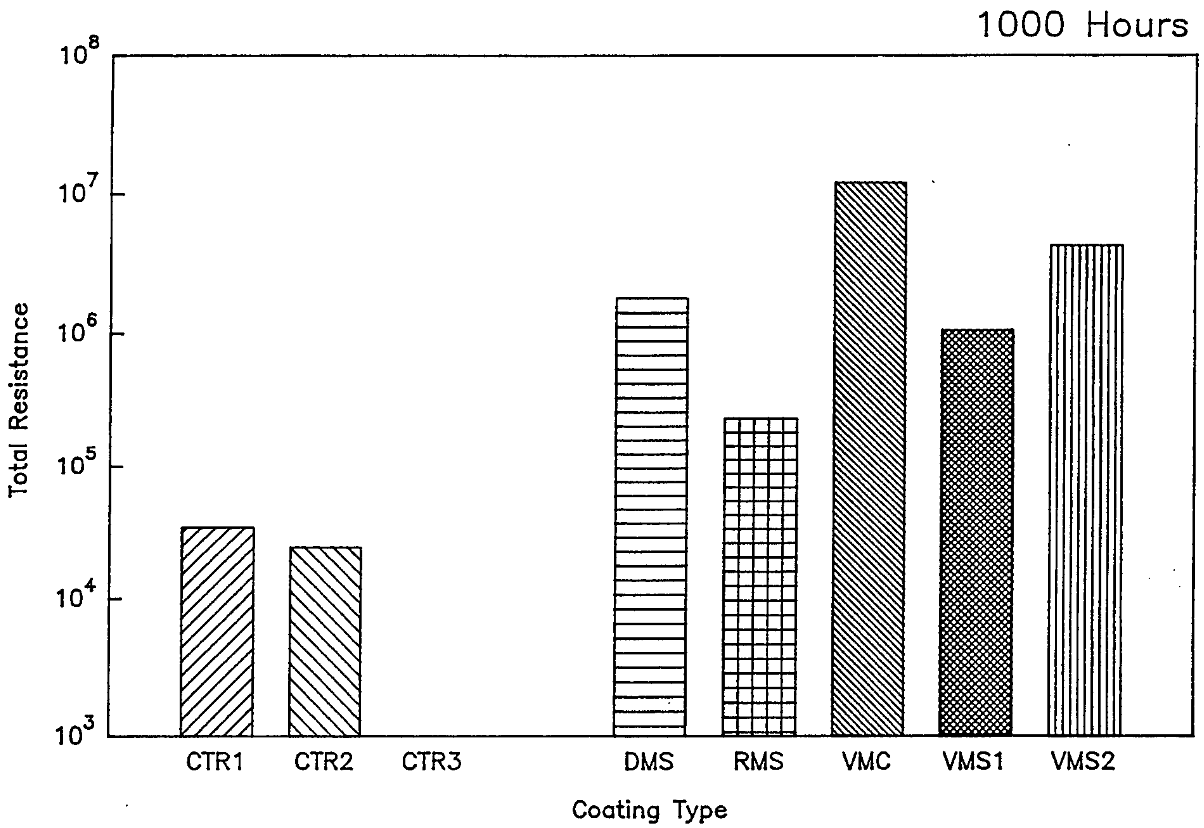


Figure A-8. Total Resistance For Various Coatings After 1000 Hours Exposure

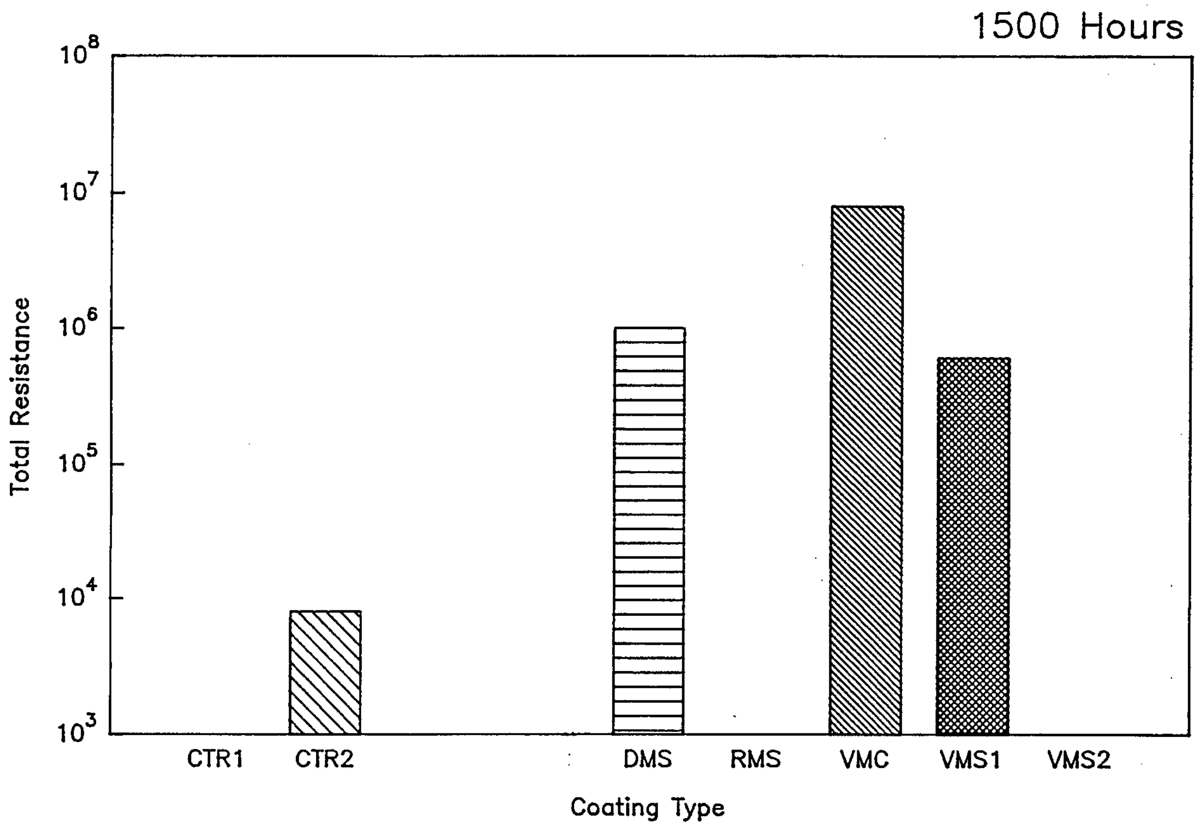


Figure A-9. Total Resistance For Various Coatings After 1500 Hours Exposure

APPENDIX B

BAR GRAPHS OF DEFECTS FROM TRAYCAN STORAGE STUDY

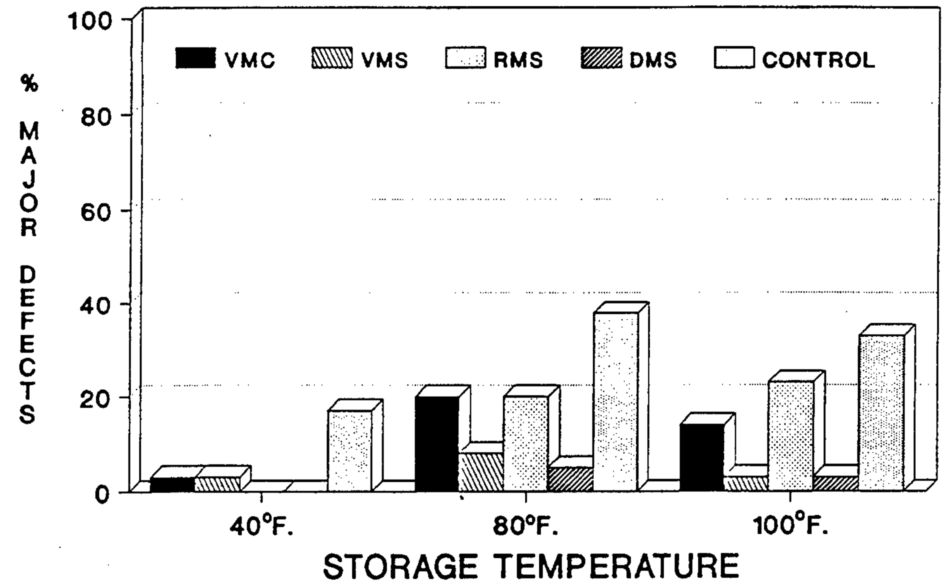


Figure B-1. Eight Weeks At 40, 80, 100°F - Cumulative.
Major Defects vs. Storage Temperature

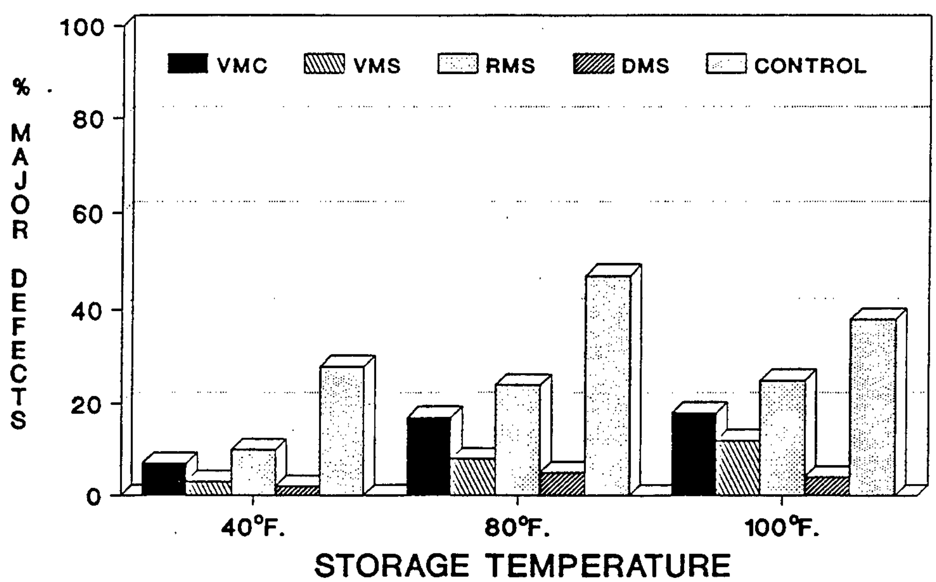


Figure B-2. Sixteen Weeks At 40, 80, 100°F - Cumulative.
Major Defects vs. Storage Temperature

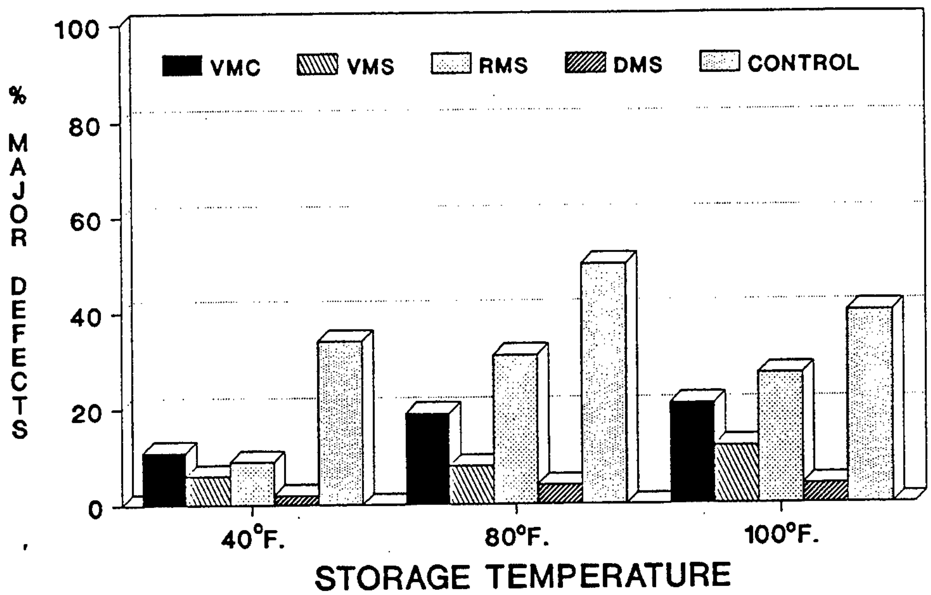


Figure B-3. Twenty-Four Weeks At 40, 80, 100°F - Cumulative.
Major Defects vs. Storage Temperature

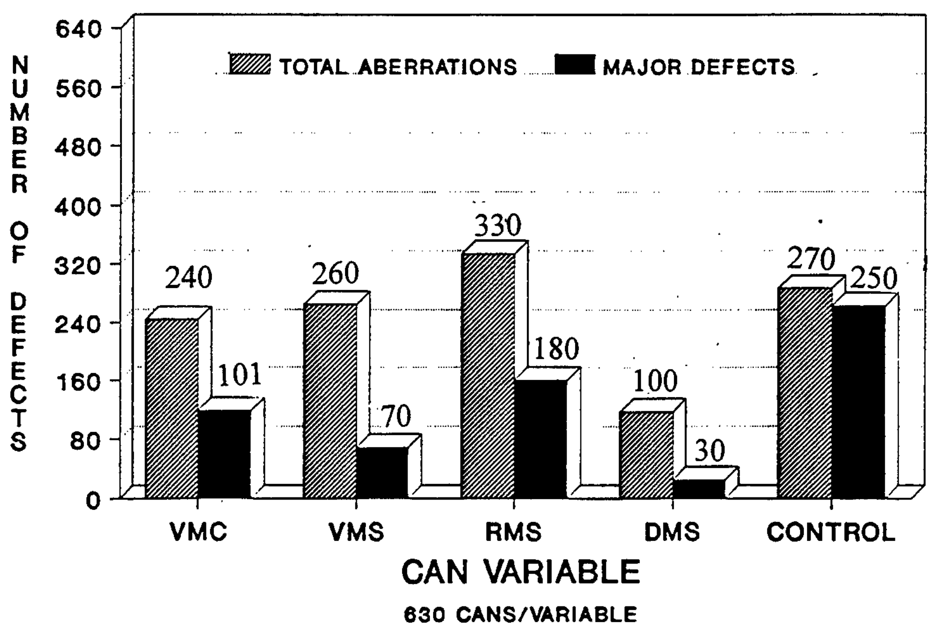


Figure B-4. Twenty-Four Weeks At 40, 80, 100°F - Cumulative.
Number of Defects vs. Can Variable (630 Cans/Variable)

SYMBOLS, ABBREVIATIONS AND ACRONYMS

AC	Alternating Current
CTR	Control (Tin-Free Steel)
DC	Direct Current
DMS	Dexter Midland Sheet
NaCl	Sodium Chloride
NRDEC	Natick Research, Development and Engineering Center
QC	Quality Control
RMS	Reliance Matte Sheet
SSCOM	Soldier Systems Command
TF	Tin-Free
TP	Tin-Plate
VMC	Valspar Matte Coil
VMS	Valspar Matte Sheet
bb	base board
cm	centimeter
e.g.	for example
g	grams
hr	hour
lb	pound
ml	milliliters
mA	milliamps
mV	millivolts
no.	number
pH	acid-base scale (log of reciprocal of hydrogen ion concentration)
v	volts
vs.	versus
#	number